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(21) International Application Number: PCT/US91/08735 (22) International Filing Date: 20 November 1991 (20.11.91) (30) Priority data: 618,448 27 November 1990 (27.11.90) US (71) Applicant: BAUSCH & LOMB INCORPORATED [US/ US]; Patent Law Department, One Lincoln First Square, P.O. Box 54, Rochester, NY 14601-0054 (US). (72) Inventor: LAI, Yu-Chin ; 23 Cooper Woods, Pittsford, NY 14534 (US). (74) Agents: POLYN, Denis, A. et al.; Bausch & Lomb Incor- porated, Patent Law Department, One Lincoln First Square, P.O. Box 54, Rochester, NY 14601-0054 (US).		(81) Designated States: AT (European patent), BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Eu- ropean patent), IT (European patent), JP, KR, LU (Eu- ropean patent), NL (European patent), SE (European patent). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: MOLD MATERIALS FOR SILICONE CONTAINING LENS MATERIALS (57) Abstract When molding shaped articles such as contact lenses from monomeric mixtures containing silicone monomers and hydro- philic monomers, the wettability of the resulting article is improved by using a mold material produced from a resin comprising a copolymer of an alpha, beta, olefinically unsaturated mononitrile and at least one comonomer to enhance melt processability.		

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MOLD MATERIALS FOR SILICONE CONTAINING LENS MATERIALSBackground of the Invention

5 This invention relates to the molding of shaped polymeric articles especially contact lenses. This invention more particularly relates to the molding of shaped polymeric materials from silicone-containing monomeric mixtures.

10

 Various molding processes are known for the production of contact lenses. Among those processes are spincasting, static cast molding, and related processes. Spincasting methods are disclosed in U.S. Patent Nos. 3,408,429 and 3,496,254. Examples of static cast molding processes are found in U.S. Patent Nos. 4,113,224 and 4,197,266. An illustration of a related molding process is U.S. Patent No. 4,555,372, which teaches a process comprising spincasting followed by lathe cutting.

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 Conventional soft contact lenses are prepared from monomeric mixtures consisting predominantly of hydrophilic monomers such as 2-hydroxyethyl methacrylate, N-vinylpyrrolidone, and others. Oxygen permeability of such conventional hydrogel materials is a result of the water content of the materials. Recently, attempts have been made to increase the oxygen permeability of soft contact lenses by the use of silicone-containing monomers. Silicone compounds are usually very hydrophobic, diminishing the wettability of silicone-containing soft lenses.

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 Another class of soft contact lenses--nonhydrogel soft contact lenses--are known as silicone elastomer lenses and are prepared from silicone rubbers. These lenses are highly permeable to oxygen and can easily

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transmit sufficient oxygen to maintain the normal respiratory process on the surface of the cornea. Unfortunately, silicone rubber is strongly hydrophobic and readily absorbs lipophilic substances which exist in the tear film. These properties result in discomfort to the lens wearer and have significantly diminished the market for this type of lens. Hydrophilic monomers have been added to silicone elastomer formulations to overcome these limitations but such attempts have not yet proven to be entirely satisfactory.

The class of contact lenses known as rigid, gas-permeable materials are also typically silicone-based copolymers prepared from siloxanylalkyl esters of methacrylic acid and other acrylate, methacrylate, or itaconate monomers in many known formulations. Such compositions, like the soft contact lens materials referenced above, exhibit enhanced oxygen permeability, due in large part to the use of silicone material. It is desirable to increase the silicone content to further enhance oxygen permeability. However, increasing silicone content diminishes wettability of the material.

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Summary of the Invention

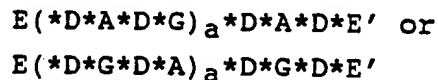
It has been found that when molding shaped articles such as contact lenses from monomeric mixtures containing silicone monomers and hydrophilic monomers, the wettability of the resulting article is improved by using a mold material produced from a resin comprising a copolymer of an alpha, beta, olefinically unsaturated mononitrile and at least one comonomer to enhance melt processability.

Detailed Description of the Invention

5 Any known contact lens material prepared from a formulation including at least one silicone monomer and at least one hydrophilic monomer may be used in the method of this invention. Included are soft contact lens formulations (both hydrogel and nonhydrogel) and
10 rigid gas permeable contact lens formulations. While the presence of both classes of monomers is deemed necessary to secure the benefits of this invention, the particular manner in which the monomers are incorporated into the polymeric composition is not
15 narrowly critical. For example, the monomers may have one or more polymerizable groups. They may be added to the final comonomeric mixture (from which the shaped article is cast) as monomers or as prepolymers.

20 Preferred soft hydrogel formulations are those described in U.S. Patent Application Serial Nos. 07/363,662 filed June 7, 1989 and 07/364,204 filed May 2, 1989, the entire contents of which are incorporated herein by reference. Other examples of
25 useable formulations are found in U.S. Patent Nos. 4,136,250; 4,740,533; 4,711,943; 4,189,546; and 4,153,641.

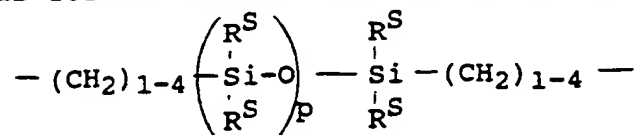
One type of presently preferred hydrogel
30 formulation incorporates prepolymers of the general formula:



35 where

- 4 -

A denotes a divalent polymeric radical represented by the general formula chosen from the group of



5

wherein R^{S} denotes an alkyl radical or a short chain fluorinated alkyl radical with 1 to 3 carbon atoms; and

p provides a moiety weight of 400 to 10,000;

10

D denotes an alkyl diradical, an alkyl cycloalkyl diradical, a cycloalkyl diradical, an alkylaryl diradical or an aryl diradical, with 6 to 30 carbon atoms;

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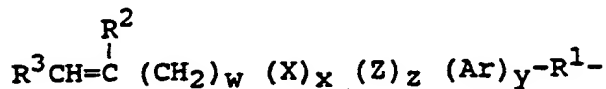
G denotes an alkyl diradical, a cycloalkyl diradical, an alkyl cycloalkyl diradical, an aromatic diradical or an alkylaromatic diradical with 1 to 40 carbon atoms which may have ether, thio, or amine linkages in the main chain;

20

* denotes a urethane or ureido linkage; and

E and E' denote polymerizable unsaturated organic radicals represented by the general chemical formula

25



wherein R^1 denotes a divalent alkylene radical with 1 to 10 carbon atoms;

R^2 denotes a -H or -CH₃ radical;

R^3 denotes a -H radical or an alkyl radical with 1 to

30

6 carbon atoms or a ---CY---R^4 radical where Y is -O-, -S- or -NH- and R^4 denotes an alkyl radical with 1 to 12 carbon atoms;

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- 5 -

X denotes $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$, or $\begin{array}{c} \text{O} \\ \parallel \\ -\text{O}-\text{C}- \end{array}$;

Z denotes -O-, -S-, or -NH-;

Ar denotes an aromatic radical with 6 to 30 carbon atoms;

a is at least 1;

w is 0 to 6;

x is 0 or 1;

y is 0 or 1; and

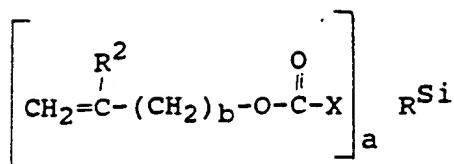
z is 0 or 1.

These propolymers are generally prepared by first reacting an aliphatic diisocyanates with a short chain diol in an aprotic solvent. After all short chain diol is consumed, a polysiloxane diol is added. After the polysiloxane diol is consumed, the reaction mixture is cooled and reacted with 2-hydroxyethyl methacrylate to complete the preparation. Preparation of a prepolymer is illustrated in the following Example 2.

These silicone-containing prepolymers may be copolymerized with a wide variety of hydrophilic monomers to produce soft hydrogel contact lenses. Hydrophilic monomers suitable for this use include 2-hydroxyethylmethacrylate, N-vinyl pyrrolidone, (meth)acrylamide, N-vinyl-N-methyl acetamide, and other olefinically unsaturated hydrophilic monomers. Further comonomers may also be added to enhance wetting or to modify other properties as is generally known to those skilled in the art.

Another presently preferred hydrogel formulation incorporates silicone-containing vinyl carbonate or vinyl carbamate prepolymers of the general formula:

- 6 -



5 wherein X denotes an -O-, -S-, or -NR³- divalent radical;

R^{Si} denotes a silicone containing organic radical;

R² denotes -H or -CH₃;

a is 1, 2, 3, or 4; and

10 b is 0 or 1.

Suitable silicone-containing organic radicals (R^{Si}) include the following:

15 $-(\text{CH}_2)_n \text{Si}[(\text{CH}_2)_m \text{CH}_3]_3;$

$-(\text{CH}_2)_n \text{Si}[\text{OSi}(\text{CH}_2)_m \text{CH}_3]_3;$

and

20 $-(\text{CH}_2)_n \left[\begin{array}{c} \text{R}^1 \\ | \\ \text{Si}-\text{O} \\ | \\ \text{R}^1 \end{array} \right]_d - \text{R}^{\text{Cl}}; \text{ and}$

25 $-(\text{CH}_2)_n \left[\begin{array}{c} \text{R}^1 \\ | \\ \text{Si}-\text{O} \\ | \\ \text{R}^1 \end{array} \right]_d - \begin{array}{c} \text{R}^1 \\ | \\ \text{Si} - \text{R}^{\text{Cl}} \\ | \\ \text{R}^1 \end{array}$

where R¹ denotes a monovalent organic radical such as an alkyl radical with 1 to 6 carbon atoms, or a fluoroalkyl radical with 1 to 6 carbon atoms;

R^{Cl} denotes

30 $-(\text{CH}_2)_p - \text{O} - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}=\text{CH}_2$

p is 1 to 6; and

d is 1-200, and

where n is 1, 2, 3, or 4, and m is 0, 1, 2, 3, 4, or 5.

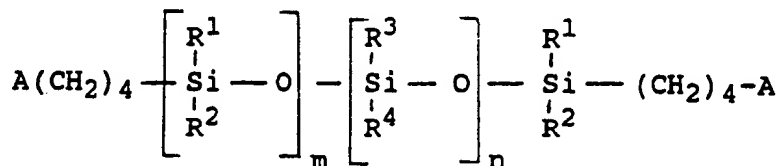
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The silicone-containing vinyl carbonate/carbamate monomers specifically include

- 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate;
 1,3-bis[4-(vinylloxycarbonyloxy)but-1-yl]tetramethyl-dis
 5 iloxane; 3-(trimethylsilyl)propyl vinyl carbonate;
 t-butyldimethylsiloxyethyl vinyl carbonate;
 trimethyl-silylmethyl vinyl carbonate;
 trimethylsilylethyl vinyl carbonate;
 2,2,2-trifluoroethyl vinyl carbonate; t-butyl vinyl
 10 carbonate; 3-[tris(trimethylsiloxy)silyl] propyl vinyl
 carbonate; 2,2,2-trifluoroethyl vinyl carbamate;
 1,1,1,3,3,3-hexafluoro-2-propyl vinyl carbonate;
 3-(vinylloxycarbonylthio)propyl-[tris(trimethylsiloxy)si
 lane]; 3-[tris-(trimethylsiloxy)silyl]propyl vinyl
 15 carbamate; "V₂D₂₅", 2,2,2-trifluoro-1-phenylethyl vinyl
 carbonate; 1-adamantane vinyl carbonate,
 1-adamantanethyl vinyl carbonate, 1-adamantaneethyl
 vinyl carbonate; and 1-adamantane vinyl carbamate.

- 20 Preferred nonhydrogel soft contact lens
 formulations are mixtures of polymerizable
 polysiloxanes containing fluorinated side chains and
 internal wetting agents. Further components such as
 toughening agents, crosslinking agents, and other
 25 auxiliary modifiers are desirably present as taught in
 U.S. Patent 4,810,764. The entire content of which is
 incorporated herein by reference.

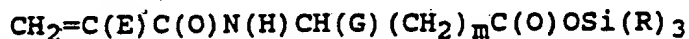
- 30 Polymerizable, fluorinated polysiloxanes employed
 in this embodiment of the invention are described by
 the general formula:



- 8 -

where A denotes an activated unsaturated group, $-R^1$ and R^2 independently denote alkyl radicals with 1 to 6 carbon atoms or phenyl radicals; R^3 and R^4 independently denote alkyl radicals with 1 to 6 carbon atoms, phenyl radicals, or fluorinated alkyl radicals with 1 to 6 carbon atoms, provided that at least one of R^3 or R^4 is a fluorinated alkyl radical with 1 to 6 carbon atoms; $m + n$ is at least 1; and n is at least 1.

Internal wetting agents ("hydrophilic monomers") useful in this embodiment of the invention include N-alkylenoyl trialkylsilyl aminates (hereinafter "NATA") (described in U.S. Patent No. 4,652,622) represented by the general formula

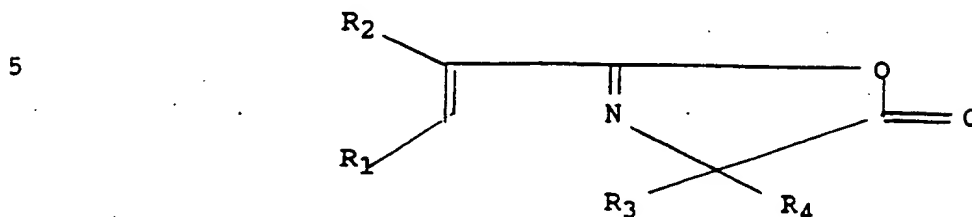


wherein

- E is H or CH_3 ,
 - G is $(CH_2)_x C(O)OSi(R)_3$ or H,
 - R is CH_3 , C_2H_5 or C_3H_7 ,
 - m is an integer from 1 to 15,
 - x is an integer from 1 to 10, and
 - $m + x$ is an integer from 1 to 15
- Acryloyl- and methacryloyl-, mono- and dicarboxylic amino acids, hereinafter NAA, impart desirable surface wetting characteristics to polysiloxane polymers, but precipitate out of siloxane monomer mixtures before polymerization is completed. NAA can be modified to form trialkylsilyl esters which are more readily incorporated into polysiloxane polymers. The preferred NATA's are trimethylsilyl-N-methacryloylglutamate, triethylsilyl-N-methacryloylglutamate, trimethyl-N-methacryloyl-6-aminohexanoate, trimethylsilyl-N-methacryloyl-aminododecanoate, and bis-trimethylsilyl-N-methacryloyl aspartate.

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The preferred internal wetting agents are oxazolones of the general formula



where

- 10 R_1 and R_2 independently denote H or CH_3 ; and
 R_3 and R_4 independently denote methyl or cyclohexylradicals.

These preferred internal wetting agents specifically include

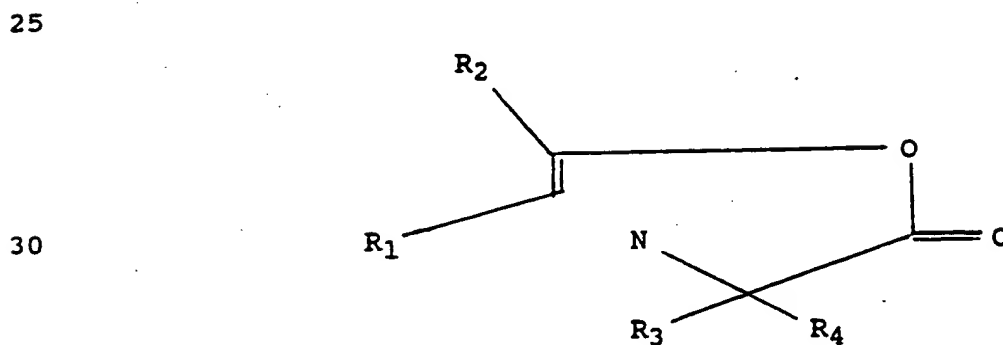
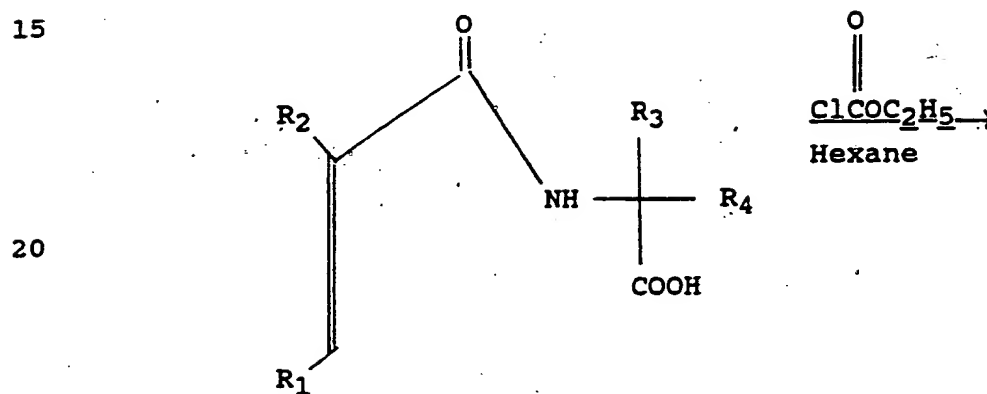
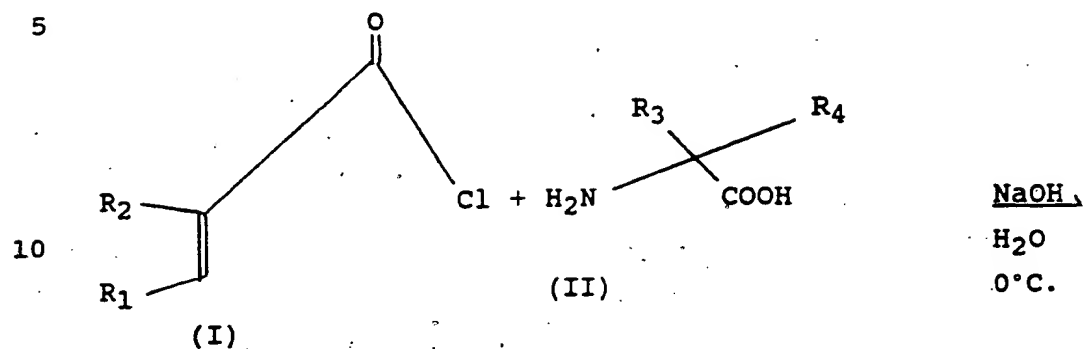
- 15 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one (IPDMO),
 2-vinyl-4,4-dimethyl-2-oxazolin-5-one (VDMO),
 cyclohexane spiro-4'-(2'-isopropenyl-2'-oxazol-5'-one) (IPCO),
 cyclohexane-spiro-4'-(2'-vinyl-2'-oxazol-5'-one) (VCO),
 20 and 2-(-1-propenyl)-4,4-dimethyl-oxazol-5-one (PDMO).

- These preferred internal wetting agents have two important features which make them particularly desirable wetting agents: (1) They are relatively non-polar and are compatible with the hydrophobic
- 25 monomers (the polysiloxanes and the toughening agents), and (2) They are converted to highly polar amino acids on mild hydrolysis, which impart substantial wetting characteristics. When polymerized in the presence of the other components, a copolymer is formed. These
- 30 internal wetting agents result through the carbon-carbon double bond with the endcaps of the polysiloxane monomers, and with the toughening agents to form copolymeric materials particularly useful in biomedical devices, especially contact lenses.

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- 10 -

These oxazolones are prepared by the general reaction sequence



- 11 -

The first step being a Shotten-Bauman acrylation of an amino acid. Upon completion of this step the polymerizable functionality is introduced by using either acryloyl or methacryloyl chloride.

5

Rigid gas permeable contact lens formulations which are suitable for the practice of this invention are silicone-based copolymers prepared from siloxanylalkyl esters of methacrylic acid and other
10 acrylate, methacrylate, or itaconate monomers in many known formulations. See U.S. Patent Nos. 4,424,328; 4,463,149; 4,664,479; and 4,686,267.

The molding resin used in this invention is a
15 copolymer of an alpha, beta olefinically unsaturated mononitrile and at least one comonomer to enhance melt processability. The resin must be stable in the presence of the unpolymerized contact lens formulation. The softening temperature is preferably at least 30°C,
20 more preferably at least 50°C to assure compatibility with cure conditions and to assure mold stability. Although the mold formed from the resin may be opaque, the ultraviolet transmission is preferably at least 10% to facilitate efficient ultraviolet curing of the
25 contact lens material.

Homopolymers of alpha, beta olefinically unsaturated mononitriles have limited application in melt processing (required for production of molds)
30 because of high melting point, poor thermal stability, and high melt viscosity. A wide variety of monomers which may be copolymerized with the mononitrile to produce resins useful for melt processing are well known in the art.

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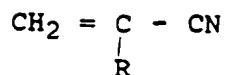
Suitable comonomers to copolymerizes with the alpha, beta olefinically unsaturated mononitriles include styrenic monomers, benzofuran, esters of (meth)acrylic acid, and vinylic monomers. Examples of
5 suitable styrenic monomers are styrene, alpha-methyl styrene, para-methyl styrene, para-t-butyl styrene, para-t-butyl monochloro styrene, and para-t-butyl dichloro styrene. Examples of suitable esters of (meth)acrylic acid are methyl acrylate, methyl
10 methacrylate, and 2-dimethylaminoethyl methacrylate. Examples of suitable vinylic monomers are vinyl acetate, 4-vinylpyridine, and vinylidene chloride. More detailed descriptions of these copolymers, their preparation, and their properties may be found in Peng,
15 F., "Acrylonitrile Polymers," Encyclopedia of Polymer Science and Engineering, 2d Ed., Vol. 1, pp. 426-470 (John Wiley & Sons, N.Y., N.Y.)(1985).

The comonomers may be modified with an elastomer,
20 desirably a copolymer of a conjugated diene and an alpha, beta olefinically unsaturated mononitrile. Particularly preferred dienes are butadiene and isoprene. Other elastomers such as acrylic elastomers, ethylene-propylene rubbers, and urethane elastomers may
25 also be employed. The only requirement of the elastomer is that it be compatible with the mononitrile.

A class of useful elastomer-modified mononitrile
30 copolymers is ABS, the two-phase system resulting when styrene-acrylonitrile grafted rubber is blended with styrene-acrylonitrile copolymers.

The olefinically unsaturated mononitriles useful
35 in the present invention have the structure

- 13 -



wherein R is hydrogen, a lower alkyl group having from
5 1 to 4 carbon atoms, or a halogen. Examples include
acrylonitrile, alpha-chloroacrylonitrile, alpha-
fluoroacrylonitrile, methacrylonitrile, and
ethylacrylonitrile.

10 Preferred resins for use in the method of this
invention are prepared by polymerizing an olefinic
nitrile (especially acrylonitrile) with an olefinic
ester (especially methyl acrylate) in an aqueous medium
in the presence of a nitrile rubber. Such resins are
15 described in U.S. Patent 3,426,102 and are available
from British Petroleum under the trademark "Barex".
Barex resin is a rubber modified copolymer containing
75% acrylonitrile and 25% methyl acrylate.

20 The surface wettability of a lens on eye is
generally accepted to refer to the wettability of the
anterior surface of the lens and not the posterior
surface which is in contact with the cornea. The
posterior surface wettability is not detrimental to the
25 performance of a contact lens as far as wettability is
concerned.

The use of mononitrile-based molding materials
disclosed in this invention is applicable to all
30 presently known, commercial molding processes,
including spin-casting, static cast molding, and spin-
casting of anterior surfaces followed by lathe-cutting
of posterior surfaces. In processes where only one
mold is required to cast lenses, the opacity of the
35 mononitrile-based mold is immaterial to curing. When
static cast molding is applied, the mold which lies

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between the light source used in ultraviolet curing and the monomer mix must be transparent enough to render acceptable curing efficiency. When heat curing is used, the opacity of the mold materials is not a concern as long as the mold is stable at the temperature applied for thermal curing.

Static casting of contact lenses conventionally requires two mold halves. The mold halves may be formed from the same or different materials. The process of this invention requires that at least one of the mold halves will be formed from a mononitrile-based resin. The mold for the anterior surface is preferably formed from a mononitrile-based resin.

While this invention has been described with particular reference to contact lenses, the method of this invention is useful in forming a wide variety of shaped articles used in biomedical applications. Such articles include dialyzer diaphragms, artificial kidneys and other implants (see U.S. Patent Nos. 2,976,576 and 3,220,960), therapeutic bandages (U.S. Patent No. 3,428,043), surgical devices such as heart valves, vessel substitutes, intrauterine devices, membranes and other films, catheters, mouth guards, and denture liners (U.S. Patent Nos. 3,520,949 and 3,618,231), and ophthalmic prostheses (U.S. Patent No. 3,679,504). Particularly preferred shaped articles for the purposes of this invention are contact lenses and preforms wherein one surface of the lens is formed in the molding process.

Contact Angle Measurement (Sessile Drop Method)

Contact angles reported in the Examples were determined according to the Sessile Drop Method first

developed by Zisman, W.A., et al., J. Colloid Sci.,
Vol. 1, p. 513 (1946). A plastic film with support was
placed on a flat plate in a Rane-Hart goniometer. A
drop of liquid of interest (distilled water, buffered
5 saline or any other liquid of interest) was applied to
the film through a metered syringe. The angle was read
from the viewer, after adjusting the baseline.

General Description of Lens Manufacturing by Static

10 Cast Molding

A monomer mix of defined composition was filtered through a disposable filter of pore size 1.2 μ into a clean vial. Through an applicator, 60-90 μ l of the mix was injected onto a clean plastic mold (for the anterior surface of a lens) and then covered with another plastic mold (for the posterior surface of the lens) and pressed gently. The molds containing monomer mix were then cured for 2-1/2 hours in the presence of ultraviolet light (4200 microwatts). The molds were opened mechanically and the molds containing lenses were put into a beaker containing an aqueous solution of ethanol or isopropanol. The lenses were released in 20 minutes. They were then extracted with an alcohol over a period of 4 to 48 hours and then boiled with distilled water. After that the lenses were put into distilled water and inspected for cosmetic quality and dimension. Those lenses that passed inspection were thermally disinfected in phosphate-buffered saline before on-eye evaluation.

EXAMPLE 1Contact Angles of Plastic Resins

5 The contact angles of plastic plaques from resins most often used in processing hydrogel lenses were measured in distilled (DI) water, buffered saline and mucin solution, using sessile drop method, with the results shown in the following table.

10	<u>Resin</u>	<u>Tradename</u>	<u>Source</u>	<u>Contact Angle (°)</u>		
				<u>DI water</u>	<u>Buffered Saline</u>	<u>Mucin</u>
15	Polyvinylchloride	Geon	Goodrich	57	66	45
	Polyetherimide	Ultem	GE	66	65	49
	Polypropylene	Polypro	Himont	66	72	54
	Polyarylate	Radel	Amoco	65	67	54
	Polybutylene terephthalate	Gafite	Celanese	57	56	50
20	Rubber-modified poly(acrylonitrile-co-acrylate)	Barex	BP	44	37	43

25 Barex resin gave the lowest contact angle in each instance, demonstrating markedly superior wettability in the test environments.

EXAMPLE 2

5 Preparation of Urethane Prepolymer Derived From
 Isophorone
 Diisocyanate, Diethyleneglycol, Polysiloxanediol
 of Molecular Weight 3000 and 2-Hydroxyethyl
 Methacrylate

10

 A 1 liter, three-neck round bottom flask equipped
with reflux condenser and nitrogen inlet unit, was
charged with isophorone diisocyanate (17.776 g,
0.08 mole), diethyleneglycol (4.2458 g, 0.04 mole),
15 dibutyltin dilaurate (0.3001 g) and methylene chloride
 (150 ml.). The content was heated to reflux. After
6 hours, the isocyanate content was checked by
titration and was found to have dropped to half of its
original amount. Then polysiloxanediol (prepared from
20 reaction of one mole of 1,3-bis(4-hydroxybutyl)
 tetramethyldisiloxane and 37 moles of dimethoxy
 dimethyl silane in the presence of acid) of molecular
 weight 3000 was added (60.002 g or 0.02 mole) and the
 content remained refluxed for 30 hours. The isocyanate
25 content was rechecked and found to have dropped to a
 quarter of the original amount. The contents were
 cooled to ambient temperature and 2-hydroxyethyl
 methacrylate (2.7301 g, 0.021 mole) was added. After
 24 hours, the isocyanate content dropped to none as
30 identified by infrared spectroscopy. The reaction was
 then suspended and the prepolymer was recovered in
 quantitative yield after stripping off the solvent.

EXAMPLE 3Stability of Acrylonitrile-Acrylate Resin
Towards Polyurethane Lens Monomer Mix

5 A lens formulation containing silicone-based
urethane prepolymer as shown in Example 2, 35 parts,
3-methacryloxypropyl tris(trimethylsiloxy)silane,
35 parts, N,N-dimethyl acrylamide, 30 parts, butyl
carbitol, 40 parts and benzoin methyl ether, 2 parts,
10 was prepared. Two drops of the liquid mix was placed
on top of a plastic plaque fabricated from Barex 210, a
copolymer containing acrylonitrile and methyl acrylate
obtained from British Petroleum. After 16 hours, there
was no change of appearance of the plaque surface,
15 indicating the plaque was stable under this test.

Similar tests were run on Ultem plaques, molded
from a polyetherimide resin from General Electric. It
was found that the surface was attacked by the same
20 monomer mix and the plaque surface became rough.

EXAMPLE 4Contact Angles of Polyurethane Monomer Mix
Cast Over Different Plastic Plaques

25 The formulation of Example 3 was cast over
silane-treated glass plates, Barex plaques and
polypropylene plaques and cured under UV. After
30 hydration of the films, the contact angles of the films
were measured. The contact angles were 52° for glass,
44° for polypropylene, and 35° for Barex cast films.
The hydrogel films cast out of Barex plaques were very
wetable by appearance.

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- 19 -

EXAMPLE 5Polyurethane Lens Surface Wettability from Clinical Testing

5 A formulation prepared as described in Example 3 (except that butyl carbitol was replaced by the same amount of n-hexanol) was cast molded into lenses, using either polypropylene or Barex molds. The lenses, after releasing, solvent extraction in ethanol for 16 hours, 10 and hydration, sterilization processes, were subjected to on-eye testings. It was found the lenses cast out of polypropylene were totally non-wetting immediately after putting on eyes, while lenses cast out of Barex molds showed good wetting characteristics.

15 Lenses of the same formulation and fabricated by spincasting in Barex molds also showed good wettability on eyes.

20

EXAMPLE 6Fluorosilicones Lenses

25 A monomer mix containing dimethacrylate-capped polysiloxane with fluoroalkyl side chains $M_2D_{35}F_{65}$ as described in U.S. Patent 4,810,764 (98 parts), octafluoropentyl methacrylate (2 parts), 2-vinyl-4,4-dimethyl-2-oxazolin-5-one (5 parts), and benzoin methyl ether (0.2 parts), was cast molded into 30 lenses with polypropylene, Radel (polyacrylate resin from Amoco), Ultem (polyetherimide resin from GE), and Barex molds. After solvent extraction in ethanol for 16 hours, hydration in boiling water for 4 hours, and inspection for cosmetic quality and dimensions, the 35 lenses were put into vials with phosphate buffered saline at pH 7.4 and thermally sterilized. The lenses

- 20 -

were then evaluated on-eye. Lenses cast in Barex molds showed consistent wettability while lenses cast in other molds were totally non-wetting, or showed serious wettability problems.

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EXAMPLE 7

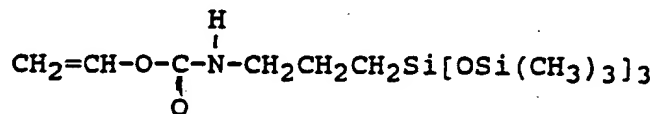
3-[Tris(trimethylsiloxy)silyl]propyl Vinyl Carbamate

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To a 200 mL 3-neck round bottom flask fitted with a magnetic stirrer, and dropping funnel was added 5.0 g (14.1 mmol) of 3-amino propyl tris(trimethylsiloxy)silane, 1.23 g (15.6 mmol) of pyridine and 50 mL of chloroform. Five minutes after adding 1.5 g (14.1 mmol) of vinyl chloroformate, an exotherm resulted. The reaction mixture was checked by gas chromatography after 10 minutes. Results showed the starting amine was consumed. The organic phase was washed once with 100 mL 2N HCl then dried with magnesium sulfate. The solvent was removed on a rotary evaporator to afford 5.8 g of crude brown oil. Following chromatography (silica gel, 50% heptane 40% methylenechloride), 5.0 g (11.8 mmol, 83.3%) of colorless oil (bp 130°C, .8 Torr) was obtained. FTIR (net, capillary) and NMR confirmed the structure

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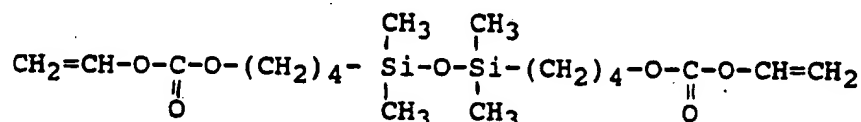
EXAMPLE 81,3-Bis[4-(vinylloxycarbonyloxy)but-1-yl]-tetramethyl
disiloxane

5 To a 500 mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, N₂ blanket, dropping funnel, and thermometer, was added 10.0 g (35.9 mmol) of 1,3-bis (4-hydroxybutyl) tetramethylsiloxane, 6.24 g (78.9 mmol) of pyridine and 100 mL of

10 chloroform. Next, 7.64 g (71.8 mmol) of vinyl chloroformate was added to the mixture dropwise producing an exotherm to 54°C. The reaction mixture was cooled to room temperature and stirred for 19 hours. The organic phase was washed twice with 100 mL 2N HCl,

15 twice with 100 mL 2N NaOH, then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, chloroform) to give 13.22 g (31.6 mmol, 88.1%) of a light yellow oil. FTIR and NMR confirmed

20 the structure



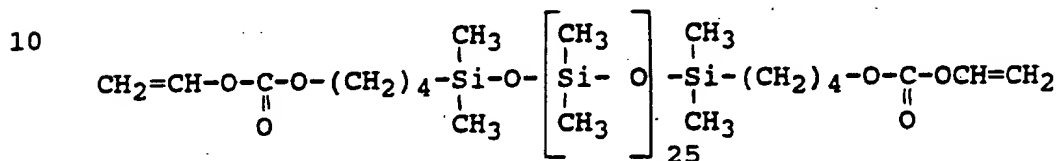
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EXAMPLE 9Preparation of "V₂D₂₅"

30 To a 100 mL 1-neck round bottom microwave flask fitted with a magnetic stirrer and a drying tube was added 5.0 g (11.95 mmol) of the tetramethyldisiloxane prepared from Example 8 and 22.15 g (74.7 mmol) of octamethylcyclotetrasiloxane. Then 0.679 g

35 (0.452 mmol) of trifluoromethanesulfonic acid was added to the reaction mixture. The reddish reaction mixture

was stirred for 24 hours, then .38 g (4.52 mmol) of sodium bicarbonate was added which resulted in foaming. After 24 hours a small amount of black solid formed. The reaction mixture was filtered through 20.0 g of activated F20 alumina to give a light yellow oil. The oil was heated at 80°C at .25 Torr for 3-1/2 hours to remove volatiles, giving 13.4 g (5.90 mmol, 49.4%) of a light yellow oil. FTIR and NMR confirmed the structure



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EXAMPLE 10Polyvinyl Carbamate Lenses

A monomer mix containing 55 parts of the monomer prepared in Example 7, 15 parts of the V₂D₂₅ crosslinker prepared as described in Example 9, 30 parts N-vinyl pyrrolidone, 15 parts nonanol, and 0.3 parts Darocure-1173 was cast molded into contact lenses using Barex, Ultem, and polypropylene molds. The lenses were released from the molds (satisfactory release could not be obtained from the Ultem molds) and then treated to remove extractibles (extracted for 48 hours with isopropanol and then with water). After sterilization, the lenses were evaluated on eye. The lenses cast in Barex molds had very good wettability whereas the lenses cast in polypropylene had poor wettability.

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What is claimed is:

1. An improved method of making shaped articles by copolymerizing at least one silicone-containing monomer and at least one hydrophilic monomer in a mold, the improvement which comprises using a mold produced from a resin comprising a copolymer of an alpha, beta, olefinically unsaturated mononitrile and at least one comonomer to enhance melt processability.

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2. The method of claim 1 wherein the shaped article is a contact lens.

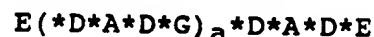
3. The method of claim 2 wherein the contact lens is a soft contact lens.

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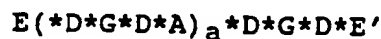
4. The method of claim 2 wherein the contact lens is a soft hydrogel contact lens.

20

5. The method of claim 4 wherein at least one silicone-containing monomer is a prepolymer of the general formula

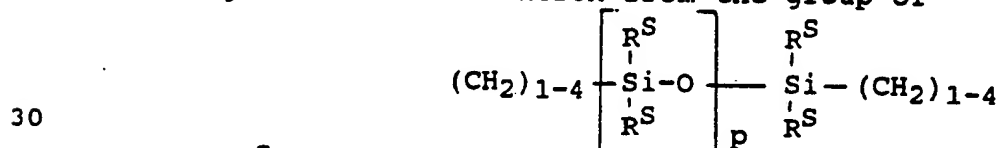


' or



25 where

A denotes a divalent polymeric radical represented by the general formula chosen from the group of



30

wherein R^S denotes an alkyl radical or a short chain fluorinated alkyl radical with 1 to 3 carbon atoms; and

p provides a moiety weight of 400 to 10,000;

35

D denotes an alkyl diradical, an alkyl cycloalkyl diradical, a cycloalkyl diradical, an

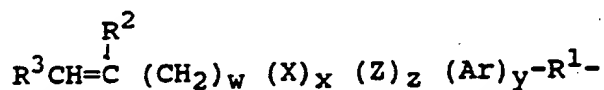
- 24 -

alkylaryl diradical or an aryl diradical,
with 6 to 30 carbon atoms;

G denotes an alkyl diradical, a cycloalkyl
diradical, an alkyl cycloalkyl diradical, an
aromatic diradical or an alkylaromatic
diradical with 1 to 40 carbon atoms which may
have ether, thio, or amine linkages in the
main chain;

* denotes a urethane or ureido linkage; and

E and E' denote polymerizable unsaturated organic
radicals represented by the general chemical
formula



wherein R¹ denotes a divalent alkylene radical with 1
to 10 carbon atoms;

R² denotes a -H or -CH₃ radical;

R³ denotes a -H radical or an alkyl radical with 1
to

6 carbon atoms or a $\overset{\text{O}}{\parallel}\text{CY-R}^4$ radical where
Y is -O-, -S- or -NH- and R⁴ denotes an
alkyl radical with 1 to 12 carbon
atoms;

X denotes $\overset{\text{O}}{\parallel}\text{C-}$, or $\text{-O-}\overset{\text{O}}{\parallel}\text{C-}$;

Z denotes -O-, -S-, or -NH-;

Ar denotes an aromatic radical with 6 to 30 carbon
atoms;

a is at least 1;

w is 0 to 6;

x is 0 or 1;

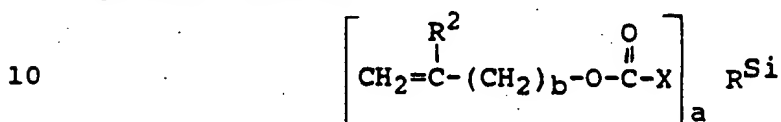
y is 0 or 1; and

z is 0 or 1.

6. The method of claim 5 wherein at least one hydrophilic monomer is selected from the group consisting of 2-hydroxyethylmethacrylate, N-vinyl pyrrolidone, (meth)acrylamide, and vinyl acetamide.

5

7. The method of claim 4 wherein at least one silicone-containing monomer is a prepolymer of the general formula



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wherein X denotes an -O-, -S-, or -NR³- divalent radical;

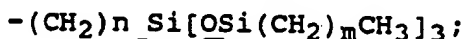
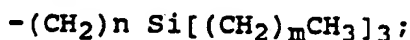
15 R^{Si} denotes a silicone containing organic radical;

R^2 denotes -H or -CH₃;

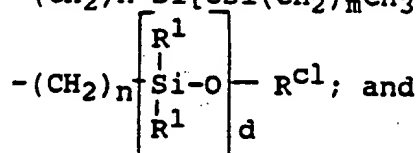
A is 1, 2, 3, or 4; and

b is 0 or 1.

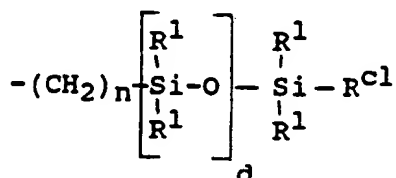
20 8. The method of claim 7 wherein the silicone-containing organic radical (R^{Si}) is selected from the group consisting of



25



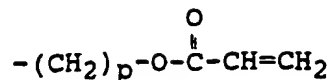
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where R^1 denotes a monovalent organic radical such as an alkyl radical with 1 to 6 carbon atoms, or a

35 fluoroalkyl radical with 1 to 6 carbon atoms;

- 26 -

R^{Cl} denotes

p is 1 to 6; and

5 d is 1-200, and

where n is 1, 2, 3, or 4, and m is 0, 1, 2, 3, 4, or 5.

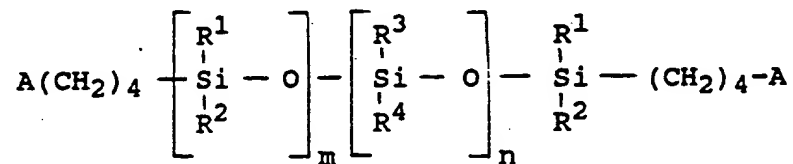
9. The method of claim 7 wherein at least one hydrophilic monomer is selected from the group
 10 consisting of N-vinylpyrrolidone, N-vinyl-N-methyl acetamide, and vinyl acetate.

10. The method of claim 2 wherein the contact lens is a soft nonhydrogel contact lens.

15

11. The method of claim 10 wherein at least one silicone-containing monomer is a polymerizable, fluorinated polysiloxane of the general formula:

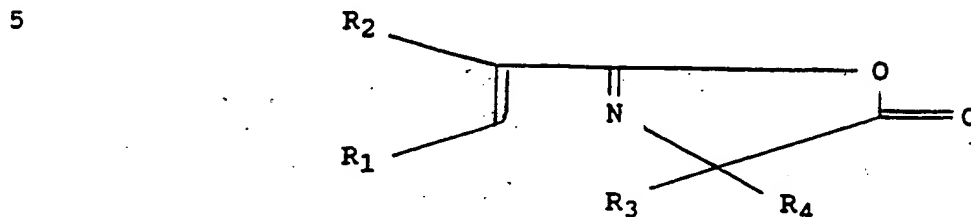
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25 where A denotes an activated unsaturated group, -R¹ and R² independently denote alkyl radicals with 1 to 6 carbon atoms or phenyl radicals; R³ and R⁴
 independently denote alkyl radicals with 1 to 6 carbon atoms, phenyl radicals, or fluorinated alkyl radicals
 30 with 1 to 6 carbon atoms, provided that at least one of R³ or R⁴ is a fluorinated alkyl radical with 1 to 6 carbon atoms; m + n is at least 1; and n is at least 1.

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12. The method of claim 11 wherein at least one hydrophilic monomer is an oxazolone of the general formula:



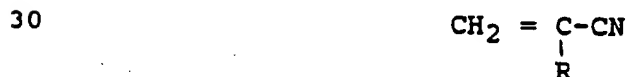
where

R_1 and R_2 independently denote H or CH_3 ; and
 R_3 and R_4 independently denote methyl or cyclohexylradicals.

13. The method of claim 11 wherein the oxazolone is selected from the group consisting of
 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one (IPDMO),
 2-vinyl-4,4-dimethyl-2-oxazolin-5-one (VDMO),
 cyclohexane spiro-4'-(2'-isopropenyl-2'-oxazol-5'-one)
 (IPCO),
 cyclohexane-spiro-4'-(2'-vinyl-2'-oxazol-5'-one) (VCO),
 and 2-(-1-propenyl)-4,4-dimethyl-oxazol-5-one (PDMO).

14. The method of claim 2 wherein the contact lens is a rigid gas permeable lens.

15. The method of claim 1 wherein the olefinically unsaturated mononitrile is described by the general formula



wherein R is hydrogen, a lower alkyl group having from 1 to 4 carbon atoms, or a halogen.

16. The method of claim 15 wherein the mononitrile is acrylonitrile.

17. The method of claim 1 wherein the comonomer is selected from the group consisting of esters of (meth)acrylic acid.

5

18. The method of claim 17 wherein the resin is prepared by copolymerizing the mononitrile with the ester in the presence of a nitrile rubber.

10

19. An improved shaped article prepared by copolymerizing at least one silicone-containing monomer and at least hydrophilic monomer in a mold, the improvement which comprises using a mold produced from a resin comprising a copolymer of an alpha, beta, olefinically unsaturated mononitrile.

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(21) International Application Number: PCT/US91/08735 (22) International Filing Date: 20 November 1991 (20.11.91) (30) Priority data: 618,448 27 November 1990 (27.11.90) US (71) Applicant: BAUSCH & LOMB INCORPORATED [US/ US]; Patent Law Department, One Lincoln First Square, P.O. Box 54, Rochester, NY 14601-0054 (US). (72) Inventor: LAI, Yu-Chin ; 23 Cooper Woods, Pittsford, NY 14534 (US). (74) Agents: POLYN, Denis, A. et al.; Bausch & Lomb Incorporated, Patent Law Department, One Lincoln First Square, P.O. Box 54, Rochester, NY 14601-0054 (US).		(81) Designated States: AT (European patent), BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Eu- ropean patent), IT (European patent), JP, KR, LU (Eu- ropean patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 9 July 1992 (09.07.92)
(54) Title: MOLD MATERIALS FOR SILICONE CONTAINING LENS MATERIALS (57) Abstract When molding shaped articles such as contact lenses from monomeric mixtures containing silicone monomers and hydro- philic monomers, the wettability of the resulting article is improved by using a mold material produced from a resin comprising a copolymer of an alpha, beta, olefinically unsaturated mononitrile and at least one comonomer to enhance melt processability.		

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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/08735

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 B29D11/00; G02B1/04; B29C33/38		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System		Classification Symbols
Int.Cl. 5	G02B ; B29C ;	B29D
Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 347 043 (PILKINGTON VISIONCARE INC.) 20 December 1989 see claims 1,10,11,12,15 see page 5, line 24 - line 29 see page 5, line 36 - line 52 see page 5, line 53 - page 6, line 20 ---	1
A	US,A,3 830 460 (JOHN O. BEATTIE) 20 August 1974. see claims 1,5,8,10,11,13 ---	1
A	FR,A,2 445 353 (COVINGTON WILLIAM S.) 25 July 1980 see claim 1 see page 17, line 39 see page 18, line 20 - line 27 --- -/-	1
<p><i>[Signature]</i></p>		
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IV. CERTIFICATION		
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12 MAY 1992	27.05.92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DEPIJPER R.D.C.	

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,3 871 803 (JOHN O. BEATTIE) 18 March 1975 see claim 1 see column 12, line 16 - line 49 see figures 5,8 see column 12, line 58 - column 13, line 2 see column 13, line 7 - line 13 ---	1

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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0347043	20-12-89	US-A- 4921205 JP-A- 2018012	01-05-90 22-01-90
US-A-3830460	20-08-74	US-A- 3931373 BE-A- 753437 DE-A- 2029098 FR-A- 2055087 GB-A- 1317005	06-01-76 14-01-71 11-02-71 07-05-71 16-05-73
FR-A-2445353	25-07-80	US-A- 4245069 CA-A- 1134983 CH-A- 648049 DE-A- 2941264 DE-C- 2954176 GB-A- 2039932 US-A- 4423195	13-01-81 02-11-82 28-02-85 17-07-80 12-06-86 20-08-80 27-12-83
US-A-3871803	18-03-75	US-A- 3806079	23-04-74

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